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厦门大学理学博士学位论文

甲烷低温燃烧反应分子筛负载 Pd 催化剂

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The Low-temperature Combustion Reaction of Methane over Pd-supported Zeolite Catalysts

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摘　要

甲烷（天然气的主要成分）是最难被氧化的碳氢化合物，并且具有比二氧化碳大得多的温室效应，因此应用于甲烷低温燃烧的催化剂研制是能源和环保领域中具有挑战性的课题。由于负载 Pd 催化剂被认为是甲烷低温燃烧活性最高的催化剂，同时 Pd 资源相对其它贵金属丰富和便宜，因而受到特别的关注。但在实际的低温燃烧应用（如甲烷尾气释放处理）中，为满足环保及经济性要求，催化剂必须在 300℃以下点燃甲烷燃烧反应并在 400℃以下使甲烷的转化率达到 100%，同时催化剂在运行状态下要求保持足够长的催化寿命。因此，目前一些氧化物负载 Pd 催化剂（如 Pd/Al_2O_3、Pd/SnO_2、Pd/ZrO_2 和 $Pd/36NiO\text{-}Al_2O_3$ 等）还难以满足要求。虽然离子交换法制备的 Pd/分子筛催化剂表现出了高的低温甲烷燃烧活性，但它们的 Pd 负载量普遍较高并表现出了差的热和水热稳定性。另外，负载 Pd 催化剂的活性与载体及添加剂的种类和性质密切相关，其活性物种的行为特点也一直是研究工作者争论的焦点。因此，开展负载 Pd 催化剂的甲烷低温燃烧研究具有重要的现实意义和理论价值。

本文首次报道了以浸渍法制备的改性 Pd/HZSM-5 催化剂应用于甲烷低温燃烧研究，并从应用基础研究的角度出发，首先从不同载体、不同 Pd 负载量、不同添加剂、不同焙烧温度和不同反应空速等方面考察了负载 Pd 催化剂的甲烷燃烧性能，同时考察了催化剂的热和水热反应稳定性，对催化剂进行了优化选择，然后主要以改性 Pd/HZSM-5 催化剂作为研究对象，利用 XRD、CO 吸附和 NH_3-TPD 技术进行了催化剂体相结构、表面 Pd 分散度和表面酸碱性的研究，利用程序升温脱附和还原、原位及非原位激光拉

曼光谱谱学技术详细地表征了负载 PdO 物种的氧化还原性能。最后，根据催化剂的甲烷燃烧活性和各种表征结果，结合相关文献，对甲烷燃烧反应机理进行了初步推测。主要研究内容和结果如下：

1. 甲烷低温燃烧催化剂的优化

首先考察了 HZSM-5、NaY、Mordenite、Al_2O_3 和 SiO_2 五种载体对负载 1wt%Pd 催化剂的甲烷燃烧反应性能的影响，证实了 Pd/HZSM-5 具有最高的催化燃烧活性，并且 Pd/HZSM-5 的 $T_{10\%}$ 、$T_{50\%}$ 和 $T_{100\%}$（甲烷转变率分别为 10、50 和 100%时的反应温度）分别比 Pd/Al_2O_3 下降了 32、96、和 70 ℃，表明 HZSM-5 载体对 Pd 催化剂的燃烧性能具有很好的促进作用，不同 Si/Al_2 的 Pd/HZSM-5，其活性没有太大的差异。

其次，0.5～4wt%Pd/HZSM-5 催化剂的活性测试结果表明：随着 Pd 负载量增高，催化剂活性的增加渐趋缓慢。

接着重点考察了具有不同添加剂的 Pd-M/HZSM-5（Si/Al_2 = 50 or 165，M = Zr、Ce、Zn、Cu、La、Ba、Fe、Mn、Ca、Mg、Li、Y、Al、Sm、Nd 和 Tb）的甲烷燃烧活性，结果表明 Zr 或 Ce 的添加显著地提高了 Pd/HZSM-5 的催化活性，使 Pd/HZSM-5 的 $T_{10\%}$ 、$T_{50\%}$ 和 $T_{100\%}$分别下降了大约 15～29、6～18 和 35～60℃；Zn 的添加对 Pd/HZSM-5 的活性基本没有影响；而其它添加剂的添加却使 Pd/HZSM-5 的活性明显降低。Pd 催化剂的甲烷低温燃烧被认为与表面 Pd-O 键的强弱有关，ZrO_2 和 CeO_2 具有大的贮氧供氧能力及高价离子的电子诱导作用，这能够减弱 Pd-O 键的强度，进而提高催化剂的燃烧活性，而其它碱性添加剂的添加使载体表面的电子密度增加，导致表面 Pd-O 键增强， 这可能是导致 Pd/HZSM-5 催化活性下降的原因。

另外，分别通过不同添加剂数量、不同反应空速和不同焙烧温度对催

化剂甲烷燃烧活性影响的对比实验，发现添加 1wt%Zr 或 Ce 对 Pd/HZSM-5 的甲烷燃烧活性具有最适宜的促进作用；Pd-Zr/HZSM-5 的催化活性对反应空速的变化（25000～76000 $mlg^{-1}h^{-1}$）不是太敏感；高温焙烧导致 Pd-Zr/HZSM-5 的表面 PdO 物种严重烧结，使催化剂的燃烧活性显著降低。

最后对催化剂在反应条件下的热和水热稳定性进行了测试，结果表明 Zr 或 Ce 的添加还有效地提高了 Pd/HZSM-5 的热和水热稳定性，说明 Pd-Zr/HZSM-5 和 Pd-Ce/HZSM-5 具有较好的甲烷低温燃烧实际应用前景。

2. 催化剂的体相结构、表面 Pd 分散度和表面酸碱性研究

催化剂的 XRD 和 Pd 分散度实验表明：Zr 或 Ce 添加剂能够促进 Pd/HZSM-5 表面产生一定的晶相 PdO，保持了催化剂表面 Pd 的相对低分散性，这说明 PdO 的适度结晶（即较大颗粒的 PdO）有利于提高催化剂的甲烷低温燃烧反应活性。同时这种结晶 PdO 还具有较好的抗高温烧结性能，这可能与 Zr、Ce 添加剂能够有效地稳定载体的比表面积有关。NH_3-TPD 实验表明强碱性添加剂（Mg 和 Li）导致 Pd/HZSM-5 的表面强酸位（主要为 B 酸位）数量严重减少，而 Zr 的添加对 Pd/HZSM-5 的表面酸性基本没有影响。结合催化剂的活性数据，发现保持催化剂表面强酸位，对改善以 HZSM-5 为载体的 Pd 催化剂的甲烷燃烧活性具有重要作用。

3. 催化剂的 O_2-TPD 和 CH_4-TPR 研究

O_2-TPD 测试发现，添加 Zr 或 Ce，使 Pd/HZSM-5 的氧物种能在更低温度脱附，明显减弱了表面 Pd-O 键的强度，而添加其它添加剂却使其氧物种在更高温度脱附，明显增强了表面 Pd-O 键的强度。CH_4-TPR 表征发现，所

有催化剂表面存在两种以上具有不同甲烷反应性的 PdO 物种，其中 Zr 或 Ce 添加剂能明显地促进 Pd/HZSM-5 中的 PdO 被甲烷还原，使起始甲烷还原峰向低温方向偏移，而其它添加剂却明显地降低了 PdO 的可还原性，其催化剂的甲烷还原峰向高温方向偏移，并且起始甲烷还原峰减小。结合催化剂的燃烧活性结果，发现催化剂的氧脱附温度、起始甲烷还原温度与它们实际的甲烷燃烧反应的起始温度具有较好的相关性，即催化剂的氧脱附温度越低，其起始甲烷还原温度越低，催化剂的实际甲烷反应的起始温度就越低。表明了 CH_4-TPR 的起始还原步骤是 PdO 催化的甲烷燃烧反应的速率决定步骤，PdO 是参与甲烷燃烧反应的活性物种。另外，Pd-Zr/HZSM-5 和 Pd-Ce/HZSM-5 的 O_2-TPD 和 CH_4-TPR 实验还发现：在 500℃焙烧，能够有效地产生足够的和稳定的具有甲烷低温氧化活性的 PdO 物种；低于 500℃焙烧，其 Pd 的氧化程度不足；而高于 500℃焙烧，则氧脱附温度和甲烷起始还原温度随焙烧温度的升高而依次升高，这说明高温焙烧引起了 Pd 催化剂的严重烧结，降低了催化剂的低温燃烧反应活性。

4. 催化剂的原位及非原位激光拉曼光谱研究

利用原位及非原位激光拉曼光谱测试进一步考察了催化剂上 Pd 物种的形态和氧化还原行为。具有不同添加剂的 Pd/HZSM-5 催化剂的非原位激光拉曼光谱结果发现，Pd/HZSM-5、Pd-Zr/HZSM-5 和 Pd-Ce/HZSM-5 三个样品表现出比其它样品更强的 PdO 特征峰（637cm^{-1}），显示出更好的 PdO 结晶性，这与它们的 XRD 和 Pd 分散度数据基本吻合，同时这种 PdO 结晶性在 400℃60min 甲烷燃烧反应处理前后没有太大的变化，说明在实际的甲烷低温燃烧反应中，PdO 具有较好的稳定性。Pd-Ce/HZSM-5 在现场氧化或甲烷还原气氛处理后的原位激光拉曼光谱测试证实，PdO 在 260℃被甲烷还

原，这与其实际甲烷燃烧反应的起始温度比较一致，说明 PdO 是甲烷燃烧反应的活性物种。同时，还原 Pd 的起始重氧化温度（240℃）低于 PdO 的甲烷还原温度（260℃），表明还原 Pd 在燃烧反应中倾向于更易重氧化，这对于甲烷燃烧反应的有效进行具有积极的意义。

5. 催化剂的甲烷燃烧机理解释

本文实验结果证实了 ZrO_2 和 CeO_2 能够通过减弱 Pd-O 键的强度而有效地提高 Pd/HZSM-5 催化剂的甲烷低温燃烧活性，PdO 中的晶格氧参与了甲烷燃烧反应。ZrO_2 和 CeO_2 具有显著的贮氧和供氧能力，使它们一方面能够接受来自毗邻 PdO 的氧而使表面易于产生氧空位，这种氧空位被认为参与了 PdO 活化甲烷的作用，另一方面，它们也能有效地提供氧到还原 Pd 上，使还原 Pd 有效地被重氧化，促进了燃烧反应的高效进行。拥有较弱 Pd-O 键的 PdO 倾向于更易产生表面氧空位。参考有关文献，本文初步地推测了 Pd-Zr/HZSM-5 和 Pd-Ce/HZSM-5 催化剂的甲烷燃烧反应机理是：CH_4 首先在具有氧空位的 PdO 表面活化并发生吸附解离，产生 CH_3 和 OH 吸附物种，接着 CH_3 依次发生吸附解离，直至产生 C 和 OH 物种，最后 C 与晶格氧反应生成 CO_2 并重新获得表面氧空位，OH 物种通过缩合反应成为 H_2O 并重新获得表面氧空位，其中 CH_4 的第一个 C-H 键的吸附解离可能是甲烷燃烧反应的速率决定步骤。在反应中消耗的氧主要通过由 ZrO_2 和 CeO_2 的氧流动性而得到补充，而 ZrO_2 和 CeO_2 所需要的氧则由与反应气之间的氧交换得到。

关键词：甲烷低温催化燃烧，改性 Pd/HZSM-5 催化剂，热和水热稳定性。

ABSTRACT

Since methane (CH_4, main constituent of natural gas) is the most difficult to oxidize among all the hydrocarbons and has a much larger greenhouse effect than carbon dioxide, low-temperature complete combustion of methane is a challenging research subject in terms of energy generation and methane emission control. Pd-related catalysts are considered as the most active ones for CH_4 combustion, and palladium metal is richer and more inexpensive than other noble metals. Thus, Pd-supported catalysts for CH_4 combustion are got an especial attention. In the practical applications, the catalyst must ignite reaction below 300 °C, oxidize nearly 100% of CH_4 below 400 °C, and possess a long catalytic lifetime. Therefore, some Pd-supported oxide catalysts, such as Pd/Al_2O_3, Pd/SnO_2, Pd/ZrO_2 and $Pd/36NiO\text{-}Al_2O_3$ etc., were not efficient enough for CH_4 combustion at low temperatures. The Pd-supported zeolite catalysts showed excellent low-temperature activity and conversion efficiency for CH_4 combustion. However, these catalysts, which were typically prepared by the ion-exchange method, included generally high Pd-loadings and still showed poor thermal and hydrothermal stabilities. In addition, there is a general agreement that the activity of Pd catalysts was greatly affected by the kinds of supports and additives. And active sites on Pd catalysts were differently described in literatures. So it is very important that Pd catalysts are researched for low-temperature combustion of CH_4 from the point of application and theory study.

In this thesis, Pd/HZSM-5 catalysts without and with additives of oxides were prepared by the impregnation method and investigated for the first time as catalysts for low-temperature methane combustion. In point of application and theory study, we optimized firstly the desired catalysts by researching into the catalytic activities and thermal/hydrothermal stabilities of various catalysts for CH_4 combustion. Then, the various characterization techniques such as X-ray

diffraction (XRD) for the crystallization of PdO on catalysts, CO adsorption for Pd dispersion of catalyst surface, ammonia temperature-programmed desorption (NH_3-TPD) for acid-basic properties of catalyst surface, oxygen temperature-programmed desorption (O_2-TPD) for oxygen desorption, methane temperature-programmed reduction (CH_4-TPR) for methane reduction of PdO, *in/ex-situ* Raman spectra for the states and redox behavior of PdO were used. Finally, reaction mechanism of methane combustion was speculated according to the activity data and characterization results of catalysts. The primary content of the research is as follows:

1. Optimization of catalysts for methane combustion at low-temperature

Pd/HZSM-5, Pd/NaY, Pd/Mordenite, Pd/Al_2O_3 and Pd/SiO_2 were investigated as catalysts for low-temperature methane combustion. Pd/HZSM-5 was found to have the best activity among these catalysts. The $T_{10\%}$, $T_{50\%}$ and $T_{100\%}$ (the temperatures corresponding to 10, 50 and 100% methane conversions) of Pd/HZSM-5 were 32, 96 and 70 °C lower than those of Pd/Al_2O_3, respectively. It was confirmed that the HZSM-5 support showed the best enhancing effect on the activity of supported PdO species than other supports. Moreover, Pd/HZSM-5 catalysts with different Si/Al_2 did not show the significant discrepancy of activity.

The activity results of catalysts with 0.5～4wt% Pd-loadings found that the low Pd content showed better promoting effect on activity of Pd/HZSM-5 than high Pd content.

Pd/HZSM-5 (Si/Al_2 = 50 or 165) catalysts without and with additives of oxides of Zr, Ce, Zn, Cu, La, Ba, Fe, Mn, Ca, Mg, Li, Y, Al, Sm, Nd and Tb were prepared by the impregnation method and were investigated for low-temperature CH_4 combustion. Addition of Zr and Ce were found to have a

significant promoting effect on the activity of Pd/HZSM-5. The $T_{10\%}$, $T_{50\%}$ and $T_{100\%}$ of Pd-Zr/HZSM-5 and Pd-Ce/HZSM-5 were found to be *ca.* 15～29、6～18 and 35～60 °C lower than those of Pd/HZSM-5, respectively. Addition of Zn was found no appreciable change to activity of Pd/HZSM-5. However, introduction of any of the other metal oxides, i.e., Cu, La, Ba, Fe, Mn, Ca, Mg, Li, Y, Al, Sm, Nd and Tb, more or less decreased the activity of Pd/HZSM-5. It was suggested that the activity of Pd-supported catalyst was related to the strength of Pd-O bond. ZrO_2 and CeO_2 possessed high oxygen storage/supplying capacity, and their positive ion with high value showed electronic inducement effect. This could weaken Pd-O bond of Pd/HZSM-5, and thus promote activity of Pd/HZSM-5. However, other basic additives could increase electronic density on Pd/HZSM-5 catalyst surface, resulting in strengthening Pd-O bond. This would decrease CH_4 activity of Pd/HZSM-5.

The amount of Zr or Ce loading affected the activity of Pd/HZSM-5, and 1 wt% Zr or Ce loading was found to be the optimum amount of additives for promoting the activity of Pd/HZSM-5 in the present catalyst systems. The gas hourly space velocity (GHSV) for methane combustion reaction did not markedly affect the activity of Pd-Zr/HZSM-5. High temperature (above 650 °C) calcination would make PdO species sinter, and thus decreased the activity of Pd-Zr/HZSM-5 catalyst.

The thermal/hydrothermal stability of both Pd-Zr/HZSM-5 and Pd-Ce/HZSM-5 were compared with that of Pd/HZSM-5 through monitoring the time dependence of CH_4 conversion over them. The results showed that Zr and Ce additives could greatly improve both the thermal and hydrothermal stability of Pd/HZSM-5. These results were critical if the Pd-Zr/HZSM-5 and Pd-Ce/HZSM-5 catalysts would be considered for practical usage in low-temperature CH_4 combustion.

2. The XRD, Pd dispersion and acid-basic properties study of catalysts

The XRD and Pd dispersion results showed that Zr and Ce additives could effectively promote to form PdO crystallites, maintain comparatively low Pd dispersion on Pd/HZSM-5 catalyst, and thus promote the presence of more reactive PdO species on both Pd-Zr/HZSM-5 and Pd-Ce/HZSM-5 for methane combustion. In the same time, these PdO crystallites still possessed better ability to resist high temperature sintering than those on other catalysts.

By NH_3-TPD experiment, we confirmed that strongly basic additives such as Mg and Li decreased markedly the strong acid (mostly B-acid) sites on Pd/HZSM-5 catalyst surface. However, Zr additive had hardly effect on the acid property of Pd/HZSM-5 catalyst surface. Combined with activity data of catalysts, one could find that the acidity of zeolite support played an important role in CH_4 combustion reaction for Pd-based zeolite catalysts.

3. The O_2-TPD and CH_4-TPR study of catalysts

The O_2-TPD tests found that Zr and Ce additives could effectively decrease the oxygen desorption temperature of Pd/HZSM-5, indicating that the Pd-Zr/HZSM-5 and Pd-Ce/HZSM-5 involved weaker Pd-O bonds than Pd/HZSM-5. However, introduction of any of the other metals, i.e., Mg, Li, La, Y, Al, Sm, Nd and Tb, increased the oxygen desorption temperature of Pd/HZSM-5, indicating that the Pd/HZSM-5 catalysts with these additives involved stronger Pd-O bonds than Pd/HZSM-5.

The CH_4-TPR tests found that there existed on the catalyst surfaces different PdO_x species, corresponding to different catalytic activities, which could react with methane. The Zr and Ce additives, among the ones we tested, seem to be the more effective in promoting the activity of PdO species of Pd/HZSM-5. Pd-Zr/HZSM-5 and Pd-Ce/HZSM-5 were found that their start-up reduction temperatures were lower than other catalysts. Combined the O_2-TPD and

CH_4-TPR results with the activity data of catalysts, one could conclude that the initial reduction step was the rate-determining process in CH_4 combustion catalysed by PdO species, and the PdO species with the lowest desorption temperature were the most reactive ones.

In addition, the O_2-TPD and CH_4-TPR tests also confirmed that the catalyst calcined at 500 °C could give birth to enough and stable PdO species for low-temperature combustion of methane. However, Pd could not be reoxidized completely when the reduced catalyst was calcined in air below 500 °C. And Pd catalyst would be sintered when calcined in air at 650 °C above, leading to the loss activity of Pd catalyst.

4. The *in/ex-situ* Raman spectra study of catalysts

The states of PdO species were also investigated by the *in/ex-situ* Raman spectra tests. The *ex-situ* Raman spectra tests found that the Pd/HZSM-5, Pd-Zr/HZSM-5 and Pd-Ce/HZSM-5 exhibited markedly stronger bands (637 cm^{-1}) of PdO phase than others, indicating the PdO crystallites on those three catalysts were apt to be formed. This is in agreement with the results of XRD and Pd dispersion. After Pd catalyst was pretreated at 400 °C for 60 min, the strength of PdO band were hardly changed, indicating that the PdO phase was stable under methane combustion reaction at low-temperature.

The *in-situ* Raman spectra tests found that PdO of Pd-Ce/HZSM-5 was reduced by methane at 260 °C. This was in agreement with the start-up reaction temperature of methane combustion of Pd-Ce/HZSM-5 catalyst, indicating that O of PdO was involved in methane combustion reaction. And the reduced Pd was reoxidized at 240 °C. This showed that the reduced Pd were apt to be promptly reoxidized under methane combustion reaction. These results had a positive role to understand methane combustion process at low-temperature.

5. The primary explain on reaction mechanism of methane combustion

In this thesis, experiment results confirmed that Zr and Ce additives could promote markedly the activity of Pd/HZSM-5 by weakening Pd-O bond, and O of PdO was involved in methane combustion reaction. ZrO_2 and CeO_2 possessed the high oxygen storage/supplying capacity. The oxygen vacancies on PdO could be formed by oxygen of PdO transfer to ZrO_2 and CeO_2. The oxygen vacancies and PdO were proposed to act as active sites for activating methane molecule. In the same time, the reduced Pd could effectively reoxidized due to the oxygen supplying capacity of ZrO_2 and CeO_2. Weaker Pd-O bonds would increase the stability and surface density of oxygen vacancies. Combined with related references, we speculated the following the reaction mechanism of methane combustion over Pd-Zr/HZSM-5 and Pd-Ce/HZSM-5.

The activation of CH_4 was supposed to occur on site pairs consisting of oxygen atoms (surface PdO) and oxygen vacancies (surface Pd) to form the dissociative chemisorption of CH_3 and OH species. Steps after the first C-H bond activation reaction involved sequential reactions of lattice oxygens of PdO with CH_x species until CO_2 was formed and desorbed. Water was proposed to form via recombination of surface hydroxyl groups. And oxygen vacancies were re-formed when CO_2 and H_2O were formed. The first C-H bond activation reaction was proposed to be the rate-determining step. ZrO_2 and CeO_2 could provide oxygen to Pd species to reoxidize the reduced Pd. In the same time, ZrO_2 and CeO_2 could get oxygen by exchanging oxygen with the mixed reaction gas.

Keywords: Low-temperature Catalytic Combustion of CH_4, The Modified Pd/HZSM-5 Catalyst, Thermal and Hydrothermal Stability.

目　录